DEVELOPMENT OF A SIMPLE DIP COATING METHOD FOR IMMOBILIZATION OF TiO_2 ONTO SOLID SUPPORTS USING DIRECT TiO_2 POWDER

by

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TABLE OF CONTENTS

CHAPTER 3 - RESULTS AND DISCUSSION

List of Tables

List of Figures

Abbreviations

E_{exc}	Excitation energy
λ	Wavelength
$\bar{\nu}$	Wavenumber
eV	Electronvolt
AOPs	Advance oxidation processes
OH●	Hydroxyl radical
UV	Ultraviolet
TiO_2	Titanium dioxide
e^-	Negatively charged electron
h^+	Positively charged hole
E_g	Band gap
Vb	Valence band
Cb	Conduction band
R	Organic compound
MB	Methylene Blue
BOD	Biological oxygen compound
COD	Chemical oxygen compound
TOC	Total organic carbon
λ_{max}	Maximum absorbance
ENR	Epoxidized natural rubber
ENR-50	50 % mole of epoxidation
ENR-25	25 % mole of epoxidation
PF	Phenol-formaldehyde resin
CBR	Cibacron Brilliant Red 3B-A
ppm	Part per million
PET	Polyethylene terepthalate
BET	Brunner-Emmet-Teller
FT-IR	Fourier transform infra red
SEM	Scanning microscope electron

EDX	Energy dispersive x-ray
TEM	Transmission electron microscope
MLC	Multilayer coating
pH_{pzc}	pH at point zero charge
AC	Activated carbon

PEMBANGUNAN KAEDAH PENYADURAN CELUP MUDAH UNTUK PENGIMOBILISASIAN TiO_2 PADA PENYOKONG PEPEJAL MENGGUNAKAN SERBUK TiO_2 SECARA TERUS

ABSTRAK

Fotomangkin titanium dioksida merupakan salah satu teknik untuk merawat air tercemar dalam memineralisasikan pencemar organik secara sempurna. Penggunaan mod penyebaran titanium dioksida semasa perawatan fotomangkin air tercemar menunjukkan aktiviti foto yang baik tetapi menimbulkan masalah untuk memisahkan mangkin yang bersaiz nano daripada air terawat. Dalam kajian ini, gabungan getah terepoksida, resin fenol dan titanium dioksida menghasilkan suatu formulasi penyaduran celup. Menggunakan formulasi TiO_2/PF/ENR, 0.15 g titanium dioksida dimobilisasikan di atas penyokong kaca. Proses penyaduran telah memberikan kebolehlekatan yang baik iaitu 63.25 % titanium dioksida masih berada di atas penyokong kaca selepas diuji dengan getaran sonik berbanding 0 % menggunakan titanium dioksida yang diimobilisasi secara teknik pemendapan. Apabila menggunakan penyokong polimer daripada akrilik, nilon, teflon, dan *polyethylene terephthalate*, lebih daripada 88 % mangkin masih tersadur di atas penyokong. Penyaduran pelbagai lapisan juga memberikan saduran yang baik dengan 94 % mangkin masih terlekat di atas penyokong kaca. Kaedah yang dibangunkan adalah ringkas, cepat, dapat mengawal ketebalan mangkin yang diimobilisasi, dapat diguna semula dan mengekalkan keaktifan fotomangkin titanium dioksida. Mangkin terimobilisasi juga dikaji dengan menggunakan mikroskop *Scanning Electron*, *Energy Dispersive X-ray*, mikroskop *Transmission Electron*, *Brunner-Emmet-Teller*, infra merah *Fourier Transform*, dan penganalisa

karbon/hidrogen/nitrat/sulphur/oksigen. Selepas 90 minit disinar menggunakan lampu pendafluor bertenaga rendah, analisa tuntutan oksigen kimia [COD] dan karbon organik total [TOC] mendapati getah terepoksida meresap ke dalam larutan sampel tetapi tidak mengganggu proses mineralisasi metilena biru. Aktiviti foto menggunakan penyaduran pelbagai lapisan meningkat lebih daripada 50 % berbanding dengan sistem konvensional penyebaran. Walaupun begitu, apabila menggunakan penapis sinaran ultra unggu, didapati pemalar kadar telah menurun secara drastik. Ini membuktikan bahawa kebocoran ultra unggu memainkan peranan penting di dalam keberkesanan penyokong pemangkin foto. Walaupun begitu, getah terepoksida didapati bertindak sebagai sensasi-foto kerana penyokong pemangkin foto di dapati masih bertindak-balas di dalam sinaran cahaya ternampakan walaupun mempunyai pemalar kadar yang amat rendah. Formulasi penyaduran celup TiO_2/PF/ENR mempunyai pemalar kadar yang baik di dalam degradasi metilena biru tetapi sebaliknya di dalam degradasi *cibacron brilliant red*. Kecekapan pemangkinan foto secara jelas dipengaruhi oleh proses penjeraban pencelup warna yang mana dipengaruhi pula oleh kehadiran cas molekul zat pewarna. Pemangkin foto terimobilisasi yang dihasilkan mempunyai kecekapan yang amat tinggi apabila gabungan proses pemangkinan foto dan proses penjeraban berlaku semasa degradasi bahan pencemar.

DEVELOPMENT OF A SIMPLE DIP COATING METHOD FOR IMMOBILIZATION OF TiO_2 ONTO SOLID SUPPORTS USING DIRECT TiO_2 POWDER

ABSTRACT

Titanium dioxide photocatalysis is one of the most promising methods for complete mineralization of organic pollutants. Dispersion of titanium dioxide during photocatalytic treatment of wastewater shows great photoactivity but requires other troublesome filtering processes to separate nano-sized catalyst from the treated wastewater. In this research, a simple dip coating method has been developed using a combination of epoxidized natural rubber, phenol-formaldehyde resin and titanium dioxide to form a coating formulation. 0.15 g catalyst was immobilized onto glass plates using coating formulation TiO_2/PF/ENR. The coating showed good adherence strength whereby after 30 seconds of ultrasonic vibration, 63.25 % of titanium dioxide catalysts still adhered onto the glass plate as opposed to 0 % using sedimentation technique. Coating adherence was even better with polymer supports like acrylic, nylon, teflon and polyethylene terephthalate with more than 88 % catalyst still remained on the plate after 30 seconds sonication. Multilayer coating involving activated carbon layer also showed excellent coating adherence with 94 % of catalyst adhered onto the supports. Therefore, the developed dip coating method was simple, fast, able to control coating thickness, reproducible and most importantly able to maintain titanium dioxide photoactivity. Immobilized catalyst was characterized using Scanning Electron Microscope, Energy Dispersive X-ray, Transmission Electron Microscope, Brunner-Emmet-Teller, Fourier Transform – Infra Red, and Carbon/Hydrogen/Nitrogen/Sulphur/Oxygen

analyzer. Chemical oxygen demand and total organic compound analyses confirmed that epoxidized natural rubber leached into the solution. However the leached rubber did not interfere with the mineralization process of methylene blue. Photoactivity using multilayer coating was better by at least 50 % as compared to suspension system. However, when ultra violet filter was applied, drastic reduction in first order rate constants were observed which indicated that leaked residual ultra violet played a major role in providing photocatalytic efficiency of the photocatalyst plates. Nevertheless, epoxidized natural rubber was found to act as photosensitizer since these photocatalyst plates responded under total visible light albeit at much smaller rate constants values. TiO_2/PF/ENR formulation was proven to possess very good first order rate constants for degradation of methylene blue but poor first order rate constant for degradation of cibacron brilliant red. Its photocatalytic efficiency was clearly influenced by adsorption process of dyes which in turn was influenced by the nature of its molecular charges. The fabricated photocatalyst in the form of multilayer titanium dioxide/activated carbon coating had the best photocatalytic efficiency due to the combination effect of photocatalysis and adsorption processes within the system.

CHAPTER 1

INTRODUCTION AND LITERATURE RIVIEW

1.1 Photochemistry

1.1.1 Definition of photochemistry

Photochemistry is a 'chemical change brought about by light' [**1**]. 'Light' means electromagnetic radiation in the visible and ultraviolet range and 'chemical change' is interpreted broadly to include most events that occur at the molecular level after absorption of photon, even if they do not lead to overall chemical change. According to Kopecky [**2**], photochemistry involves reactions of molecules in their electronic ground state which is the lowest electronic energy state. A molecule in its ground (unexcited) state can absorb a quantum of light energy, or photon, and go to a higher-energy state, or excited state. Such a molecule is then much more reactive than a ground-state molecule and can undergo entirely different reactions than the more stable molecule, following several different reaction pathways [**2**].

There are two important principles of photochemistry [**1**]:

1. *Grotthuss-Drapper law*: only light absorbed by a molecule can be effective in bringing about chemical change.
2. *Stark-Einstein law*: the primary photochemical act involves absorption of just one photon by a molecule.

The energy required for electronic excitation is the *excitation energy* (E_{exc}), which is inversely proportional to the *wavelength* (λ). In experimental photochemistry, wavelength (λ) in nanometers (nm) and energy in kJ or kcal are preferred while in spectroscopic and theoretical studies; *wavenumber* $\bar{\nu} = 1/\lambda$ (cm^{-1}) and *electronvolt* (eV) are usually used [**2**].

1.1.2 Application of Photochemistry

Natural phenomena of photochemical processes are not only essential for life but also beneficial in technological procedures. Most of photochemical processes are advantageous and cover many technological methods and their products are commonly used in daily life [**2**]. The applications of photochemistry are shown in Figure 1.1.

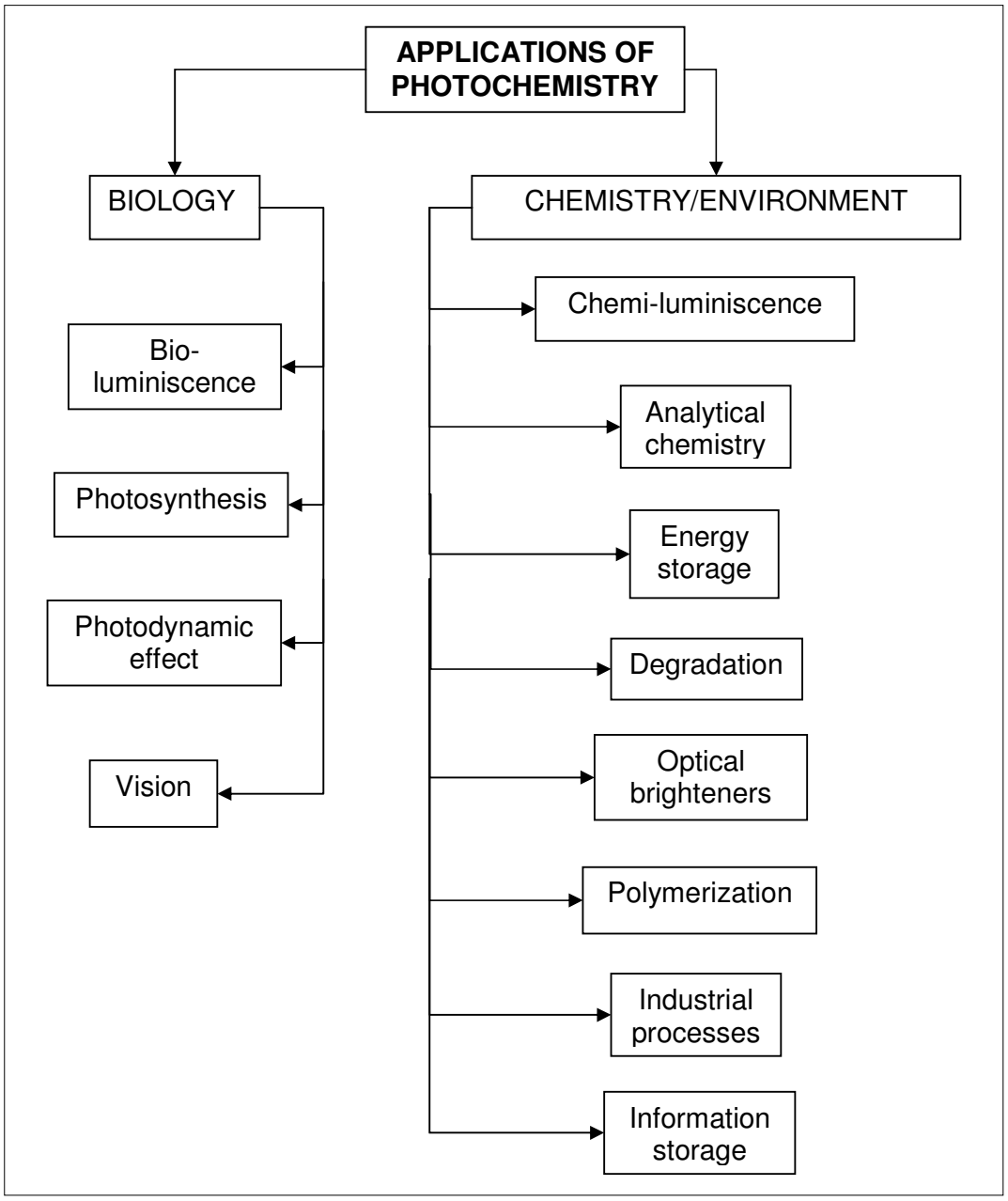

Figure 1.1: Application of Photochemistry (as modified from Kopecky [**2**])

1.2 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are alternative techniques of destruction of harmful organic pollutants from wastewaters. These processes involve chemical oxidation processes using hydrogen peroxide (H_2O_2), ozone (O_3), combined ozone & peroxide, hypochlorite, Fenton's reagent, ultra-violet enhanced oxidation such as UV/O_3, UV/ H_2O_2, UV/air , wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant) [**3, 4, 5**].

AOPs have been applied for destructing hazardous organic chemicals in water, destroys the contaminants through an oxidative breakdown initiated by a powerful oxidizing species such as hydroxyl radicals [**5, 6**] which are the most powerful oxidizing species after fluorine [**4**].

1.2.1 Process of AOPs

AOPs increase the rate of an oxidation process by the use of highly reactive species, the most widely used being the hydroxyl radical, •OH, which can increase a reaction rate by a million to a billion times. Basic oxidation processes involve the conversion of a chemical state of a contaminant to a higher level of oxidized products (some standard oxidizing agents used are O_3, O_2, air or H_2O_2). These radicals subsequently react with the contaminants and through a series of multi-step reactions form the end products such as low molecular weight carboxylic acids that are biodegradable, non-toxic, and unregulated for surface discharge. Complete mineralization to CO_2, H_2O, and

residual ions such as Cl^-, if chlorinated contaminants are involved, is achievable, if necessary [**7**].

1.2.2 Applications of AOPs

AOPs can be applied to many processes involving contaminated industrial wastewater, groundwater, drinking water, ultrapure water and process water. Many applications have been for groundwater remediation and the removal of volatile and semi-volatile organic compounds such as chlorinated alkenes, ethers, chlorinated alkanes and pesticides. AOPs are also applied for the treatment of industrial wastewater and removal of phenolic compounds, COD, cyanides and ketones. These compounds are commonly encountered in wastewater generated from various industries such as the explosives, resins, wood preservation, aerospace, and electronic industries [**5**].

Conventional wastewater treatment is based upon various mechanical, biological, physical and chemical processes. This is a combination of many operations like filtration, ultrafiltration, flocculation, coagulation, adsorption on activated carbon, reverse osmosis, sterilization, active sludge or chemical oxidation on organic pollutants [**4, 6, 8**]. After filtration and elimination of particles in suspension, biological treatment is needed and the post treatment of the adsorbent materials or solid wastes is necessary and expensive. The drawbacks of these methods are the creation of phases with more concentrated pollutants and unfortunately not all organic pollutants are biodegradable [**6,8**].

Among the AOPs, heterogeneous photocatalysis has appeared as the most promising destructive technology leading to the total mineralization of most organic pollutants [**8, 9**]. In most cases, the degradation is conducted for dissolved compounds in water with UV-illuminated TiO_2 powder [**9**].

1.3 Heterogeneous Photocatalysis

1.3.1 Definition of heterogeneous photocatalysis

According to Fox and Dulay [**11**], heterogeneous photocatalysis involves electron-hole pair formation initiated by band-gap excitation of a semiconductor particle. Upon photoexcitation of several semiconductors nonhomogeneously suspended in either nonaqueous, or in gaseous mixtures, simultaneous oxidation and reduction reactions occur. Molecular oxygen is often assumed to serve as the oxidizing agent. The incident light that initiates this sequence is in a wavelength region (the visible or low-energy range of ultraviolet regions of the spectrum) absorbed by the semiconductor rather than by the substrate of interest. These reactions involve photosensitization.

Heterogeneous photocatalytic processes can be defined as catalytic processes during which one or more reaction steps occur by means of electron hole pairs photogenerated on the surface of semiconductor materials illuminated by light of suitable energy [**12**].Some steps of a photocatalytic process are redox reactions involving the photogenerated electron-hole (e^- - h^+) pairs.

Initial interest in photoinduced redox reactions was prompted by Fujishima and Honda's 1972 discovery that water could be split (simultaneously oxidized and reduced) upon illuminating a TiO_2 single crystal electrode to which a small electrochemical bias had been applied [**11**]. Since then, extensive research had been done focusing on the production of hydrogen from water using solar illumination to generate a combustible fuel. Unfortunately, no significant progress has been made since 1980s but a second attractive application was proposed that a similar approach could be used for degrading organic compounds presents in water or air steams [**13**].

1.4 Titanium Dioxide, TiO_2

1.4.1 TiO_2 as semiconductor photocatalyst

Semiconductors can act as sensitizers for light induced redox-processes due to the electronic structure of the metal atoms in chemical combination. It is characterized by a filled valence band and an empty conduction band. Various types and characterization of selection semiconductor materials are shown in Table 1.1. Photocatalysis by semiconductors is the result of the interaction of electrons and holes generated in an activated solid with the surrounding medium. Activation is the consequence of light absorption [**13**]. Electron hole pairs are formed in the solid particle that can recombine or participate in reductive and oxidation reactions that lead to the decomposition of contaminants [**3, 13**]. The powder form of TiO_2 is shown in Figure 1.2.

Figure 1.2: Titanium Dioxide powder

Among many semiconductors investigated, titanium dioxide (TiO_2) in anatase form has become a standard in environmental applications because it proved to be efficient, biologically and chemically inert, inexpensive, resistant to photocorrosion and chemical corrosion, non toxic, highly photoactive, recyclable and has suitable band gap (E_g = 3.2 eV) in which its redox potential of the H_2O/•OH couple (-2.8 eV) lies [**7, 14, 15**]. These properties make TiO_2 a main candidate for broad applications.

1.4.2 Crystallographic structure of TiO_2

There are two structures of TiO_2 photocatalyst: rutile and anatase.

Each titanium ion is at the centre of an oxygen octahedron in both of the structures. The oxygen ions form a slightly distorted hexagonal compact lattice in rutile while in anatase, the oxygen form a cfc lattice. Each oxygen has three coplanar near neighbour titanium cations in both rutile and anatase structures.

In rutile, the three Ti – O –Ti angles are roughly equals to 120° but one of angles in anatase is about 180° while the other two are close to 90°. The

structures of TiO_2 are shown in Figure 1.2 and the physical properties are shown in Table 1.2 [**10**].

Table 1.1: Band gaps for selected semiconductor materials [**10**]

Materials	Band gap (eV) at 300 K
Diamond	5.47
Si	1.12
Ge	0.66
α - Sn	0.07
α - SiC	2.99
AlSb	1.58
GaSb	0.72
GaAs	1.42
GaP	2.26
InSb	0.17
InAs	0.36
CdS	2.42
CdSe	1.7
CdTe	1.56
ZnO	3.35
ZnS	3.68
PbS	0.41
PbSe	Not Available
PbTe	0.31
TiO_{2-x} (rutile) (anatase)	3.03 3.2
$BaTiO_{3-x}$	2.5 – 3
Cu_2O	2.1
$Mn_{1-x}O$	Not Available
$Li_xMn_{1-x}O$	Not Available
AgCl	Not Available
SnO_2	3.6

Table 1.2: Physical properties of rutile and anatase TiO_2 [**10**]

	Rutile	**Anatase**
Band-gap energy	3.03 eV	3.2 eV
Electron effective mass	$m^* = 20m_0$	$m^* = 1m_0$
Hall mobility (electron, room temperature)	0.1 $cm^2/(V\ s)$	4 $cm^2/(V\ s)$
Dielectric Constant		
ε_s ($\perp$ c)	89	31
ε_s (‖ c)	173	170

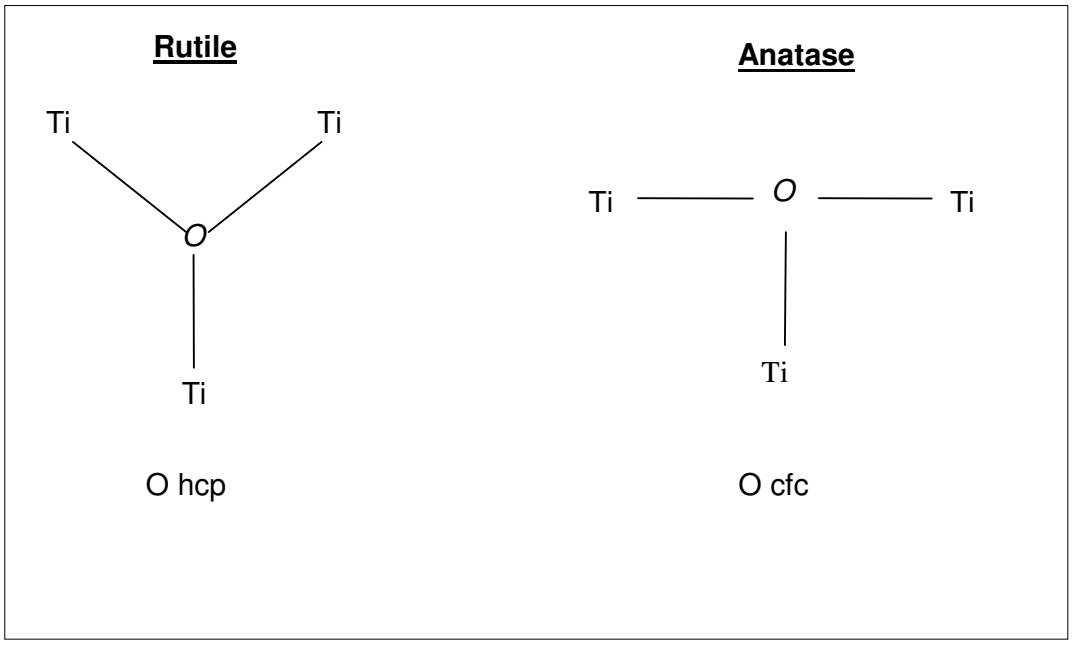

Figure 1.3: Structures of TiO_2 [**10**]

1.4.3 General mechanism of TiO_2 photocatalysis

The basic process of photocatalysis is ejecting an electron from the valence band (vb) to the conduction band (cb) of the TiO_2 semiconductor when it is excited with ultraviolet light (λ < 380 nm).This is due to irradiation of TiO_2 with energy equal or more than the band gap energy of Titania (> 3.2 eV for anatase). The photoexcitation promotes an electron (e^-) from the valence band and leaves an electronic vacancy or hole (h^+) in the valence band [**16**]. Thus the act of photoexcitation generates an electron-hole pair:

$$TiO_2 + hv \rightarrow e^-_{cb} + h^+_{vb} \quad (1.1)$$

These species undergo charge transfer reactions across the interface with oxygen, water or organic pollutants adsorbed on TiO_2 surface [**19**]. In the valence band, the holes produced by irradiation migrate to the interface and reacts with OH^- adsorbed onto the TiO_2 to create hydroxyl radicals (•OH) which are powerful oxidants to attack the recalcitrant organic compound (R) of interest (as modified from Robert and Malato [**8**], Dijkstra [**20**] and He and Gong [**21**]):

$$h^+_{vb} + H_2O \rightarrow \bullet OH + H^+ \quad (1.2)$$

$$h^+_{vb} + OH^- \rightarrow \bullet OH \quad (1.3)$$

$$h^+_{vb} + R_{ads} \rightarrow R^+ \quad (1.4)$$

The ejected electrons react with electron acceptors such as oxygen adsorbed or dissolved in water [**6**]:

$$e^-_{cb} + O_2 \rightarrow O_2^{\bullet -} \quad (1.5).$$

The electrons and holes may recombine together without electron donors or acceptors:

$$e_{cb}^{-} + h_{vb}^{+} \rightarrow TiO_2 \qquad (1.6)$$

The mechanism of TiO_2 photocatalysis is shown in Figure 1.4.

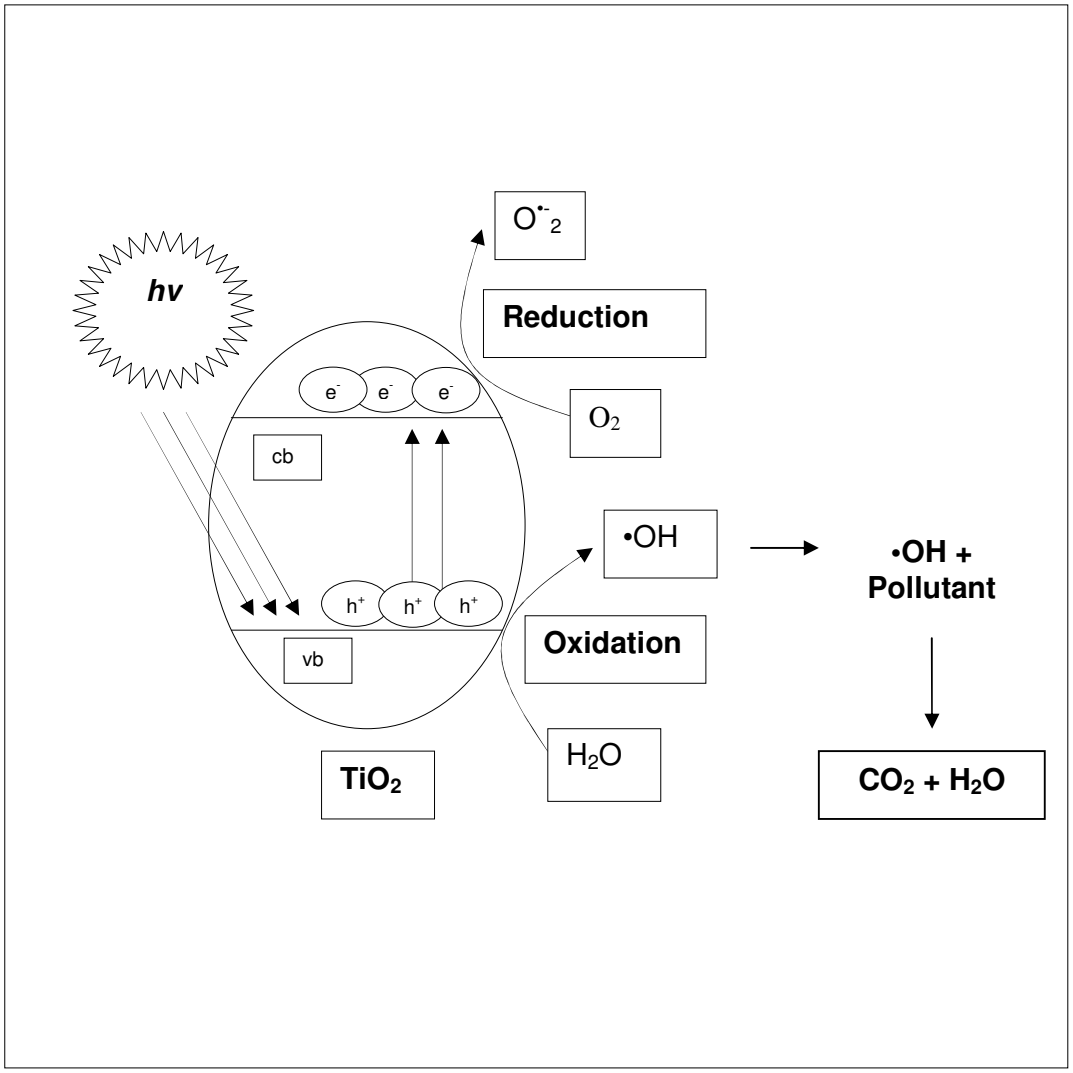

Figure 1.4: General mechanism of TiO_2 photocatalysis (as modified from Robert and Malato [**8**], Dijkstra [**20**] and He and Gong [**21**])

1.4.4 The present state of photocatalyst development

Applications of TiO_2 photocatalyst can be divided into five areas:

1. Fog proof and self cleaning glass

A combination of a titanium dioxide photocatalyst and hydrophilic silicon material will form a thin layer of water when exposed to UV light which is called a super-hydrophilic phenomenon. This feature is attractive for the application for architectural or automobile windows and mirror [**22**].

2. Anti-bacterial, anti-viral and fungicidal

TiO_2 photocatalyst has strong ability as disinfectant, decomposes and removes the dead germs or toxins. It will only generate antibacterial effect when exposed to light [**25**].

3. Anti-soiling, self cleaning

The photocatalytic activity of Titania in thin coatings of the material will exhibit a self cleaning and disinfecting properties when exposed to UV radiation [**24**]. These properties make the material a candidate for applications like medical devices, food preparation surfaces, air conditioning filters, and sanitary ware surfaces [**24**].

4. Deodorizing, air purification

In the process of treating air streams, TiO_2 must be suspended on some sort of surface to allow the gas to pass over it and react. This is usually some sort of matrix with a high surface area, which the UV light is shown upon [**25**]. An air

treatment system for ethylene removal has been developed. This system will be placed in produce sections of grocery stores to remove the naturally occurring ethylene that causes fruits and vegetables to spoil [**25**]. TiO_2 is also deposited on tiles for the elimination of bad smells and atmospheric pollutants and on inorganic fibres for photocatalytic air-cleaning [**23**].

5. Water treatment, water purification

In photocatalytic degradation, hydroxyl radicals (•OH) are generated when the photocatalyst is illuminated in the presence of water and air [**26**]. These ultra reactive species associated with oxygen are able to achieve a complete mineralization or organics pollutants into carbon dioxide, water and other non-toxic products [**6, 26, 27**]

1.5 Immobilization of TiO_2

Titanium dioxide semiconductor is the most widely used in environmental applications due to its high activity. In order to enhance the photoactivity, TiO_2 particles should be so small to offer high number of active centres by unit mass [**33**]. Conventional photocatalytic studies have been carried out with TiO_2 dispersions in aqueous solutions. Unfortunately, the aqueous suspension of powder TiO_2 is limited for industrial application due to the high cost of filtration process to remove the catalyst particles [**19, 27, 32, 33**]. This problem can be solved by immobilizing the catalyst on various supports.

Many techniques were proposed for the immobilization of TiO_2 on solid supports like glass, glass beads, quartz, silica, activated carbon, fibreglass cloth, zeolites, stainless steel, ceramics, clothes, monolith, and polymer membranes [**9, 19, 35, 36. 37**]. The major drawback of immobilized TiO_2 is the decrease of its specific surface area [**9**].

Immobilization of TiO_2 can be prepared by many deposition techniques such as sol-gel, atmospheric pressure metal organic chemical vapour deposition, electron beam evaporation, reactive magnetron sputtering, spray pyrolysis, electrophoresis, anodic oxidative hydrolysis of Ti^{3+}, reactive thermal deposition and static-dynamic films compressed method [**38, 39, 40**]. Table 1.3 summarises the photocatalytic processes of immobilized TiO_2.

Several research works using ENR to immobilize TiO_2 photocatalyst have been established before the outcome of this study. Lim [**28**] had immobilized titanium dioxide photocatalyst using electrophoretic method in the degradation of diuron. TiO_2 could be immobilized quickly and easily via this method using small amount of ENR and methanol as solvent. The support used was carbon coated polyethylene terephthalate plastic (or PET) which acted as a conductor in TiO_2 immobilization. Lin [**29**] also had done research about electrophoretic deposition of TiO_2. In his work, tungsten oxide has been added in the coating solution to enhance the photodegradation of methylene blue. Both works done by Lim and Lin utilized visible light as the energy source.

Table 1.3: Photocatalytic processes of immobilized TiO_2

Compound	Supports	Catalyst	Spectral range	Coating Method
MB, Reactive red 2	Glass beads	TiO_2	UV	Deposition: Glass tube dipped in TiO_2 suspension, heated 572 ℃, 3 h [**14**].
Copper	Stainless Steel plate	TiO_2	UV	Electrophoretic deposition [**30**].
Lead	cPET	TiO_2,	UV	Electrophoretic deposition [**31**].
Rhodamine B	Titanium plate	Titania films	UV	Etched Ti samples, rinsed with ethanol and H_2O_2, dried at 80 ℃, 3 days [**17**].
	Glass slides	TiO_2	UV	Reactive magnetron sputtering [**32, 41**].
	Glass, Indium tin oxide glass, ρ-type monocrystalline film	TiO_2	UV	Dip coating [**42**].
	Glass	TiO_2	UV	Sol gel [**43**]
Methyl Orange	Glass slides	Au/TiO_2	UV	Electron beam evaporation [**18**]
H-acid	Cuddapah Stone	TiO_2	UV	Spray technique using acrylic emulsion [**19**].
MB, Orange G, Alizarin S, Azo-Methyl Red, Congo Red	Glass	TiO_2	UV	Sol-gel: Used titanium isopropoxide and isopropanol [**9**].
Orange G, Orange II, Congo Red, Indigo Carmine, Malachite Green, Ramazol Blue, Methyl Yellow	Glass	TiO_2/H_2O_2	UV	Deposition: TiO_2 suspension (pH 3) poured on etched glass plate, dried at 100℃, calcined at 435 ℃ [**26**].

Table 1.3 continued

MB, Acetaldehyde	Non-alkali glass	TiO_2	UV	Reactive magnetron sputtering [**22**].
Basic Blue 41, Basic Red 46, Hemicyanine	Glass slide	TiO_2	Visible light	Reverse micellar route using Triton X-100 and TTIP consist of uniformly sized [**44**].
3-NBSA, Acid Orange-7	Pumice stone pellets	TiO_2	UV	Impregnation on pumice stone, fixed on cement/ polycarbonate sheet [**37**].
Acid Brown 14	Alumina and glass beads	TiO_2	Solar	Etched beads submerged in TiO_2 suspension, dried 120℃, 24 h [**45**].
Methyl Orange	Soda lime glass	TiO_2/PEG	UV	Sol gel: Used polyethylene glycol (PEG) as alkoxide solution [**46**].
MB	Foamed Polyethylene sheet	TiO_2	UV	Thermal bonding: Scrapped PE film dipped in TiO_2 suspension, sandwiched with Al foil and pressed by hot iron, air dried [**47**]
	Buoyant Polystyrene beads	TiO_2	UV	Thermal attachment procedure: TiO_2 suspension and polystyrene beads mixed together before dried at 200 ℃, 18 min [**48**].

Table 1.3 continued

Phenol	Activated carbon, AC	TiO_2	UV/Solar	AC homogenized with TTIP and isopropyl alcohol to form polymerized gel and repeated 4 times before calcined 300 – 350 ℃, 5h [**49**].
	Tiles	TiO_2/Zeolite	UV	Spray technique to form thin film using acrylic emulsion [**36**].
	Ti plate	TiO_2/Ti	UV	Sol gel: Used $Ti(OBu)_4$ and ethanol [**18**].
	Aluminium plate	TiO_2	UV	Electrophoretic deposition [**50**].
	Glass-drum/pipe	TiO_2/Pt	UV/Solar	Water glass spread to outer layer of glass pipe, dried at 80 ℃. TiO_2/Pt spread by spray gun to the rotating glass pipe, dried at 450 ℃, 1 h [**51**].
	Glass fibres	TiO_2/Pt	UV	Sol gel: Used $Ti(OBu)_4$ and ethanol [**52**].
2-chlorophenol, penta-chlorophenol	Quartz tube	TiO_2/dopants	UV	MOCVD: doped with Nd^{3+}, Pd^{2+}, Pt^{4+} [**15**].
p-nonylphenol, polyethoxylate (NPE-9)	Flexible fibreglass cloth	TiO_2	UV	Paste: TiO_2 dispersion loaded onto fibreglass cloth using paint brush, dried and calcined 200℃. Sol gel: TTIP and ethanol, calcined 200 ℃ [**53**].
2-4-dichlorophenol	Glass slide	TiO_2/Triton X-111	UV	TiO_2, EDTA and Triton deposited onto glass with adhesive tape strip [**40**].
4-chlorophenol	Conducting glass	TiO_2 colloids	UV	Sol gel: Used Titanium tetraethoxide and alcohol [**54**].

Table 1.3 continued

Methyl ethyl ketone	Glass, non-woven cellulosed synthetic fibers, pyrex glass plate	TiO_2	UV	Sol gel: Used TTIP and isopropanol [**55**].
Methyl-tert butyl-ether (MTBE)	Soda lime glass	TiO_2	UV	Dip coating: Glass dipped in TiO_2/ethanol suspension, heated 120 ℃, 20 min [**56**].
Acetaldehyde	Quartz cell	TiO_2/dopants	UV	Photodeposition method: To prepare Pt, Pd, Ag loaded in TiO_2 [**57**].
Trichloroethylene	Plastic optical fibers	TiO_2	UV	Dipping and drying: Supports dipped in TiO_2 suspension at pH 4.5, dried 24 hours [**58**].
	Glass plate	TiO_2	UV	Sol gel [**59**].
	Glass beads	TiO_2	UV	Etched beads submerged in TiO_2 suspension, dried 120 ℃, 1 hr and washed with water [**60**].
Ethylene	Borosilicate glass rings	Titania films	UV	Sol gel: Used TTIP and HNO_3 [**61**].
Trichlorobenzene	Indium-tin oxide glass	TiO_2/Ni-PTFE	UV	Sol gel, electrophoretic deposition to incorporate PTFE and photodeposition [**62**].
Triethylamine	Glass slides	TiO_2	UV	Dip coating: Etched glass dipped in TiO_2 suspension, dried and repeated 8 times [**63**].

Table 1.3 continued

Aniline	Porous nickel	TiO_2/Ni	UV	TiO_2 and PVA coated on porous nickel substrate. Polyvinyl alcohol as binder [**64**].
Formic, glycolic, citric acid	Stainless steel	TiO_2	UV	Physical Vapour Deposition (PVD) [**65**].
3-NBSA, 4-nitrotoluene, sulfonic acid	Porous lava	TiO_2	UV	TiO_2 slurry impregnated on pumice stone, dried 100 ℃ overnight [**27, 66**].
Benzene	Glass	TiO_2	UV	CVD method [**67**].
	Pyrex glass plate	TiO_2/Zeolite	UV	Sol gel [**68**].
Formic acid	Glass tube	TiO_2	UV	Dip coating: Cleaned glass tube dipped in TiO_2 suspension, dried, dipped and annealed at raising temperature to 573 K, 3 h [**24, 31**].
Butane	Vycor tube	TiO_2 , ZnO	Solar	Spray pyrolysis [**39**].
Oestrogen compounds	Ti-6Al-4V alloy	TiO_2	UV	Electrophoretic [**28**].
Atrazine	Glass rings	TiO_2 colloids	UV	Sol gel [**35**].
Diuron	Glass plate	TiO_2	UV	Deposition method [**69**].
Cyanides	Silica	TiO_2	UV	Sol gel: Titania supported over porous silica [**33**].

Table 1.3 continued

4-Chlorobenzoic acid	Rotating disk	TiO_2 composite ceramic balls	UV	TiO_2 ceramic balls screwed on the disk [**70**].
Isoproturon	Glass rings	TiO_2	Solar	Sol gel [**71**].
Benzoic acid	Stainless steel	TiO_2	UV	Electrophoretic [**72**].
Solid phase PVA	Unsupported composite film	PVA-Pt/TiO_2	UV	Electrospinning method [**21**].

1.6 Methylene Blue & Textile Wastewater

1.6.1 Wastewater from textile processing

Textile manufacturing is one of the largest industrial producers of wastewater and many studies have been published on wastewater from textile operations. Sources for chemical pollution from textile wet processing includes dyes and pigments, specialty chemicals, commodities (including water), and incoming substrates. The largest pollution source is the incoming substrates. There are a considerable number of specialty processing assistants, as well as commodity chemicals that are used to prepare, colour and finish greige fabrics. Specialty chemicals are proprietary mixtures of commodity chemicals and surfactants designed to accomplished specific purposes in processing [**73**].

Surfactants are very important components of nearly every chemical processing assistant. Surfactants are widely used in textiles for a multitude of

purposes. Most surfactants find their way into the wet processing wastewater at some point. They are the important contributors to aquatic toxicity, BOD, COD, and TOC in textile wastewater.

There are four basic classifications of textile surfactants: (i) cationic, (ii) anionic, (iii) nonionic, and (iv) amphoteric. In many cases, surfactant is applied to the fiber for rewetting, lubricity, anti-static, or other purposes. In other cases, the surfactant affects the processing solution in some way, such as stabilization of an emulsion or dispersion.

Surfactants are the major source of aquatic toxicity and in order to avoid this problem, toxic surfactants must either be eliminated from used or degraded via biological and chemical treatment. Surfactants vary very widely in their characteristics with respect to biodegradation; therefore, surfactant substitutions in textile processes have a great effect on wastewater treatment, as well as residual toxicity after treatment [**73**].

1.6.2 Treatment of dye-containing wastewater

Dyes in general are not readily biodegradable and because dyes are intensely coloured, a small amount in wastewater is noticeable. However, the effect is more displeasing rather than hazardous. Wastewaters from dye manufacturing plants and dye-houses are treated before leaving the plant [**34**].

Biological treatment is the most common technique used in effluent treatment. There are two types of treatment, aerobic and anaerobic. The aerobic needs air for the bacteria to perform degradation process on the activated sludge. Anaerobic bacteria operate in absence of air. Activated sludge removes only 10 – 20% of the colour [**34**].

Activated carbon is very effective in removing low concentration of soluble chemicals including dyes and its main drawback is its limited capacity. Activated carbon is best for removing colour from dilute effluent [**26, 34**].

Chemical treatment of the effluent with flocculating agent is generally the most efficient way to remove colour. The process involves adding a flocculating agent such as ferric (Fe^{3+}) or aluminium (Al^{3+}) ions to the effluent. This induces flocculation. A coagulant may be added to assist the process. The final product is a concentrated sludge [**8, 34**].

Chemical oxidation involving advance oxidation processes is one of the latest techniques to treat chemical effluent. This procedure uses strong oxidizing agents such as ozone, hydrogen peroxide, chlorine or potassium permanganate to force degradation of more resistant organic molecules. These treatment are expensive and of limited scale [**7, 8, 34**].

1.6.3 Methylene Blue

Dyes and pigments are classified according to their structure or to the methods by which they are applied to the substrates such as in dyeing and printing textiles, leather and fur dyeing, in paper manufacture, in the mass coloration of plastics and as paints and surface coatings. The same chromophoric system may be present in dyes and differing widely in usage and application, the presence or absence of solubilizing groups, proton-accepting groups, long-chain alkyl groups, being among the factors determining dyeing characteristics for a certain technical purpose [**74**]. The classification of dyes according to their constitution was explained by Abrahart [**74**].

Methylene Blue (MB) is classified under Thiazine group. The molecular structure of MB is shown in Figure 1.5 and the properties of MB are summarized in Table 1.4. The maximum absorbance (λ_{max}) of MB is around 661nm-665nm. Methylene Blue is a cationic dye. It becomes ionized in aqueous solution and form a positively charge chromophore. The chief member of Thiazine is Methylene Blue, produced from the simple starting material *N,N*-dimethylaniline by means of a number of interesting chemical stages [**74**].

The first step is the nitrosation of dimethylaniline followed by reduction with zinc dust or aluminium powder and acid to diamine. The diamine is oxidized in aqueous solution with sodium dichromate in presence of sodium thiosulphate giving the thiosulphonic acid. Further oxidation in the presence of an equimolecular proportion of dimethylaniline gives an indamine. Further